Characteristic Chain-End Racemization Behavior during Photolysis of Poly(L-lactic acid)

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ABSTRACT

Photolysis of poly(L-lactic acid) (PLLA) has many unclear points, such as the degradation mechanism, kinetics, products, and racemization mechanism. To clarify these features of PLLA photolysis, the relationship between photolysis and racemization was examined. The hexad stereosequential analysis of photodegraded PLLA was investigated to specify the racemized positions within a chain in comparison with hydrolysis and thermal degradation. Results from ^{13}C NMR spectra of UV-irradiated PLLA samples indicated that the samples have racemized D-lactate units at chain-ends. From the comparison of racemization behavior among photolysis, hydrolysis, and thermal degradation, it was confirmed that the preferential racemization behavior of each of these three degradation processes is characteristic and distinct, being identified as chain-end racemization, poor racemization, or internal-unit racemization, respectively. The characteristic chain-end racemization behavior of photolysis was first confirmed in this study.

KEYWORDS

poly(L-lactic acid) / photolysis / racemization / stereosequence / stereoregularity

INTRODUCTION

Poly(L-lactic acid) (PLLA) is an aliphatic polyester derived from renewable resources such as starch. PLLA is a well known recyclable material because of its ability to undergo a reversible conversion between PLLA and L-lactic acid/L-lactide by polymerization and depolymerization, respectively. In terms of reactivity, the hydrolysis and pyrolysis of PLLA have been widely investigated. However, the photolysis of PLLA has not been studied in detail,[1-9] leaving many unresolved areas for further investigation, such as the degradation mechanism, kinetics, products, and the racemization mechanism. When the optical purity of PLLA is lowered by the racemization, its crystallizability decreases and most of its useful properties are lost.[10] Thus, to be practically useful, PLLA must have a high enough optical purity.

Previously, the photolysis of PLLA has been investigated with various light sources such as a medium pressure Hg lamp,[1-3] Xe lamp,[4] long-wavelength UV lamp,[5] Xe/Hg continuous wave lamp,[6] black light,[7] Xe-F pulsed excimer laser,[8] and an open flame carbon-arc lamp.[9] PLLA exhibits strong absorption bands below 250 nm,[6] originating from absorption by a carbonyl group. Although original PLLA exhibits very weak absorption in a range of »=250-310 nm, the absorption increases with UV irradiation using a medium pressure Hg lamp under air.[11] Sakai et al. conducted a photosensitized reaction to PLLA photolysis with N,N,N',N'-tetramethyl-*p*-phenylenediamine as a photosensitizer, which gave rise to a new absorption in a range of 250-370 nm, resulting in the main-chain scission of PLLA.[6]

It has been proposed that the photolysis mechanism of PLLA proceeds via the "Norrish type photo cleavage", especially the Norrish II type reaction, based on increases in absorptions at 3290 and 990 cm^{-1} for ½$_{OH}$ and ½$_{C=C}$ of hydroxyl and acrylic groups, respectively, in IR spectra.[11] Thus far, however, no information has been provided for either a typical absorption of ½$_{C=C}$ at around 1640 cm^{-1} in the IR spectra or for characteristic signals in the ^{1}H NMR spectra for the acrylic group. Moreover, two random decomposition kinetics, i.e. autocatalytic[9] and non-autocatalytic,[7] have been tentatively applied to calculate the photolysis rate constant without these kinetics being verified. Very few characterization results of photolysis products have been given and little information on the racemization provided

except for details of the changes in molecular weights of residual polymers. Sakai et al.[6] proposed other degradation mechanisms based on electron spin resonance (ESR) studies, in which the UV degradation of PLLA comprised a dissociation reaction at the RCOO-R• bond followed by the dehydrogenation of ±-hydrogen on an asymmetric carbon. Bocchini et al.[2] and Gardette et al.[3] investigated the photo-oxidation of PLLA under air and proposed a mechanism based on hydroperoxide decomposition and resulting anhydride formation.

In our previous report,[12] to obtain more details of PLLA photolysis, UV-C light (» = 253.7 nm) was chosen as the UV source and used to directly excite the carbonyl group of PLLA. To assess quantitatively relationships between the chain scission and racemization, molecular weights of irradiated PLLA were precisely estimated. An interesting finding from quantitative analyses of the exact molecular weight and monomeric unit composition, was a close correspondence between the chain scission ratio and the generated D-lactate unit ratio, which increased in parallel during the first 0-120 min of irradiation. This suggested that approximately one D-lactate unit was generated for every chain scission. From a mechanistic consideration, it was presumed that the racemization equilibrium occurred at both carboxyl and hydroxyl chain ends, where the racemization converted the original L-lactate units into D,L-lactate units.

To clarify the relationship between photolysis and racemization, the specification of racemized positions in a chain is very important. One approach to such specification is the stereoregularity analysis of degraded polymer chains. So far, stereoregularity analysis of polymers has been used to specify controlled structures of polymer chains synthesized with various specific catalysts. In the stereoregularity analysis of poly(D/L-lactic acid), the tetrad and hexad stereosequence sensitivity on ^{1}H and ^{13}C NMR spectra have been employed.[13-17] Interestingly, one important feature suggested by the reported hexad stereosequence sensitivity of carbonyl carbon was that on the ^{13}C NMR spectrum end-racemo sequences: *siiii* and *iiiis* alone showed signals of C(=O) at lower chemical shift positions than that of the isotactic sequence: *iiiii*.[14] Other stereosequences showed their signals at higher chemical shift positions than that of the isotactic sequence.[16] Considering degradation mechanisms, changes in the

stereosequence sensitivity of degraded polymer chains must give effective information about the relationship between chain scission and racemization.

Therefore, in this report, the hexad stereosequential analysis of photodegraded PLLA was undertaken to specify the racemized positions, at which the chain scissions were assumed to occur. Moreover, to verify the aspects of PLLA photolysis, features of other degradation methods: hydrolysis and thermal degradation were also analyzed in order to compare with the photolysis.

EXPERIMENTAL SECTION

Materials. Monomers: L-lactide (L-unit 99.6%, melting point 97°C) and D,L-lactide (L-unit/D-unit 50/50, melting point 124°C) were received from Musashino Chemical Laboratory, Ltd. (Tokyo, Japan) and Tokyo Chemical Industry Co., Ltd. (TCI, Tokyo, Japan), respectively, and purified by two cycles of recrystallization from toluene before use. After the purification, meso-lactide as a main impurity was not detectable by gas chromatography (GC). Catalyst: 2-ethylhexanoate ($Sn(Oct)_2$) was purchased from Wako Pure Chemical Industries, Ltd. (Wako, Osaka, Japan) and used as received. All the solvents were commercially obtained and used as received.

Poly(L-lactic acid) (PLLA) (M_n 72300, M_w 128000, lactate unit ratio L/D=98.5/1.5, optical purity 97.0 ± 0.06%) was prepared by a ring-opening polymerization of L-lactide with $Sn(Oct)_2$ in a previously reported manner[18] and purified by a dissolution-precipitation method using a chloroform-hexane system. Poly(D,L-lactic acid) (PDLLA) (M_n 12000, M_w 26000, lactate unit ratio L/D=49.4/50.6) was prepared by a ring-opening polymerization of D,L-lactide with $Sn(Oct)_2$ at 120°C for 1 h, and purified by the dissolution-precipitation method using a chloroform-hexane system.

PLLA film preparation. PLLA film was prepared by a compression molding method with a heat-pressing machine IMC-180C (Imoto Machinery Co., Ltd. (Kyoto, Japan)) at 200°C/7MPa for 8 min, resulting in a transparent film (thickness=120 ± 20 μm). Molecular weight of the obtained PLLA film was measured with a size-exclusion chromatograph as being M_n 39000 and M_w 71000.

Test samples were cut out from the film as squares (50×50 mm^2) for photolysis and hydrolysis, and as strips (50×2 mm^2) for thermal degradation.

Photolysis of PLLA. Photolysis of PLLA samples was performed under air according to a previously reported method.[12] A 15 W UV-C sterilizing lamp (»$_c$ = 253.7 nm, half breadth < 5 nm; Sankyo Denki Co., Ltd. (Kanagawa, Japan), model GL-15) was used as an irradiation source. Film samples were irradiated at 36 ± 7 °C and 37 ± 3 % RH for prescribed times up to 5 days in a chamber, providing shielding from external irradiations. Film samples were placed at right angles to the direction of irradiation. Irradiation intensity, which was measured with a TOPCON (Tokyo, Japan) UV-C radiometer UVR-T1, was controlled at 4.3 $mW \cdot cm^{-2}$. The experiment was carried out three or four times with reasonable reproducibility.

High-pressure steam hydrolysis of PLLA. Hydrolysis of PLLA samples was carried out with high-pressure steam according to a previously reported method.[19] The high-pressure steam hydrolysis of PLLA film samples was carried out in an autoclave (Tomy (Tokyo, Japan) autoclave model SS-325, unobstructed capacity 55L) at 120°C/0.202MPa.The internal temperature of the autoclave was thermostated to within ±0.5°C. After autoclaving for prescribed periods, the PLLA samples were dried under vacuum at room temperature for one night. Each hydrolysis experiment was repeated three or four times.

Thermal degradation of PLLA. Thermal degradation of PLLA samples was carried out according to a previously reported method.[20] A PLLA film sample (70 mg) was put in a NMR sample tube (5 mmÆ). The sample tube was melt-sealed by a burner under vacuum. The sample was heated in a silicon oil bath thermostated at 200°C. After a prescribed time ranging from 1 to 5 h, the sample tube was quenched at 4°C in a water-bath, and then opened by cutting the glass. Chloroform-*d* (0.63 mL) was added to

dissolve the heat-treated PLLA film sample for ^{13}C NMR measurement. Each heat treatment experiment was repeated three or four times.

Characterization. Changes in the stereoregularity of PLLA samples after the photolysis, hydrolysis and thermal degradation were evaluated by ^{13}C NMR and high performance liquid chromatography (HPLC) analyses. Number and weight average molecular weights (M_n and M_w) of the treated samples were measured by size exclusion chromatography (SEC).

^{13}C NMR spectra were measured on a 125-MHz JEOL JNM-ECP500 FT-NMR spectrometer at a setting temperature 40 °C. Chloroform-*d* was used as a solvent and the chemical shifts were reported as ´ values (ppm) relative to internal tetramethylsilane (TMS) unless otherwise noted. The ^{13}C NMR spectrum of a 10 wt/v-% $CDCl_3$ solution of PLLA was acquired using proton decoupling. A total of 32,768 data points were obtained at a spectral width of 31.25 KHz. The recycle time was set at 2.88 s, and 10,000 scans were performed. The ^{13}C NMR measurement was repeated three times with reasonable reproducibility.

Optical purity of lactate units was analyzed using a HPLC method according to a previously reported procedure[12]: A PLLA sample (10 mg) was degraded by ammonolysis and dissolved in a 25% ammonia solution (2 mL) by stirring overnight at room temperature. After dissolving completely, the solution was concentrated by evaporation under vacuum to remove the ammonia and water. The residue was then dissolved in distilled water to prepare a monomer solution (0.1 wt/v-%) for the optical purity measurement. The optical purity of the dissolved lactic acids was measured on a Shimadzu high pressure liquid chromatograph LC-10A equipped with a UV detector SPD-10A VP. Optical resolution chromatography was conducted using a ligand exchange column MCI GEL CRS10W at 30 ºC and 2mM-CuSO4 eluent (0.5 $mL \cdot min^{-1}$). Calibration curves for L and D-lactic acids were prepared by using the standard D/L-lactic acids obtained from Wako Pure Chemical Industries, Ltd.

Molecular weights of PLLA samples were measured on a TOSOH HLC-8120 SEC system with refractive index (RI) and ultraviolet (UV, » = 254 nm) detectors under the following conditions: TSKgel

Super HM-H linear column (linearity range, $M_{n,PSt}$ = 5.89 × 10^2 - 2.00 × 10^6; molecular weight exclusion limit, $M_{n,PSt}$ = 4 × 10^8), $CHCl_3$ (HPLC grade) eluent at a flow rate of 0.6 mL·min^{-1}, and column temperature of 40ºC. Calibration curves for SEC analysis were obtained using polystyrene standards with low polydispersity values ($M_{n,PSt}$ = 5.89× 10^2, 7.70 × 10^2, 2.43 × 10^3, 3.68 × 10^3, 1.32 × 10^4, 1.87 × 10^4, 2.93 × 10^4, 4.40 × 10^4, 1.14 × 10^5, 2.12 × 10^5, 3.82 × 10^5, 5.61 × 10^5, 2.00 × 10^6, Aldrich). The sample (15 mg) was dissolved in chloroform (3 mL) and the solution filtered through a membrane filter with a 0.45 mm pore size. The SEC traces were evaluated by a universal calibration method (UCM) using the published Mark–Houwink–Sakurada constants for PLLA and polystyrene at 40 ºC as follows:[12]

PLLA : $[\cdot] = (2.068\times10^{-4})M^{0.734}$

Polystyrene : $[\cdot] = (2.072\times10^{-4})M^{0.655}$

Based on UCM, the linearity range and molecular weight exclusion limit are $M_{n,UCM}$ = 4.41 × 10^2 - 1.03 × 10^6 and 1.6 × 10^8, respectively. In the following sections, the $M_{n,UCM}$ and $M_{w,UCM}$ were expressed simply by M_n and M_w.

Prediction of chemical shift values by molecular orbital calculations. Chemical shift values of carbonyl carbons on hexamers of lactic acid having different tacticities were calculated by a molecular orbital method. All computations were done on a Dell Dimension DIMC521, equipped with 2.20GHz Athlon 64 processor board with use of a Hulinks Spartan ’06 (Wavefunction, Inc. (USA)). Geometries of the hexamers were optimized by the Hartree-Fock/3-21G* method. Chemical shift values of carbonyl carbons on ^{13}C NMR spectra were then predicted by the program.

RESULTS AND DISCUSSION

Changes in Molecular weight and Optical purity during Photolysis of PLLA. In the previous report,[11] it was confirmed that the molecular weight of UV-C irradiated PLLA sample notably decreased in the initial period of 0-120 min according to the homogeneous non-autocatalytic random degradation

kinetics. An important feature was that from the quantitative analyses of molecular weight and monomeric unit composition, ratios for both the PLLA chain scission and the generated D-lactate unit increased in parallel during the irradiation, suggesting that approximately one D-lactate unit formed for each chain scission.

Figure 1 shows changes in M_n and M_w of the UV-C irradiated PLLA film samples for 5 days (0-120 h) alongside non-irradiated reference samples. In Table SI-1 in Supporting Information, all the results are listed. The M_n and M_w values rapidly decreased within 1day, whereas those of the reference samples scarcely changed, clearly indicating that the decreases were due to UV-C irradiation.

In order to confirm the degradation kinetics of the photolysis, the changes in M_n and M_w values of irradiated samples were analyzed according to the auto-catalytic and non-auto catalytic random degradation kinetics. As shown in Figure 1, the logarithmic plots of M_n and M_w values for the auto-catalytic degradation kinetics[21] were curved, not linear, whereas the plot between $t^{4/3}$ vs. $t^{1/3}/M_w$ for the non-auto catalytic random degradation kinetics[22] exhibited a linear relationship (Figure 2b). However, another plot between t vs. $1/M_n$ for the auto-catalytic random degradation kinetics showed a suppressive curve, not a linear relationship (Figure 2a). This lack of linearity in the plot using M_n is due to the difficulty in applying random degradation kinetics, based on statistical prediction, when moving into a low molecular weight region (<500), because the linearity range of the column is $M_n = 4.41 \times 10^2$ - 1.03×10^6. Considering the previously demonstrated accuracy of the M_w value in comparison with the M_n value on a degradation process,[19] it can be assumed that based on the plot using M_w the main reaction of the photolysis in the time range of 5 days proceeds according to the non-auto catalytic random degradation kinetics.

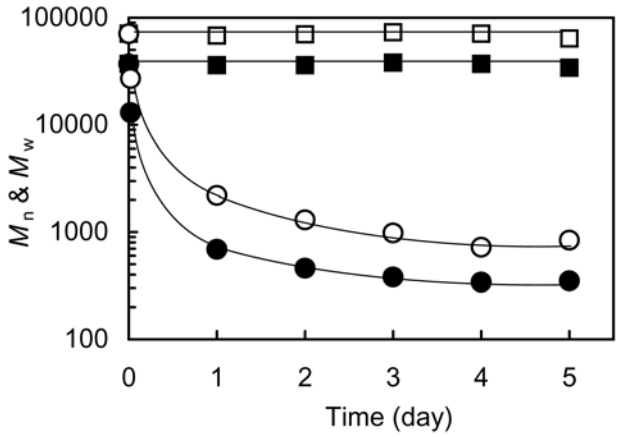

Figure 1. Changes in M_n and M_w values of PLLA with UV-C irradiation. M_n Ï , M_w Ë; Reference M_n , Reference M_w ¡ .

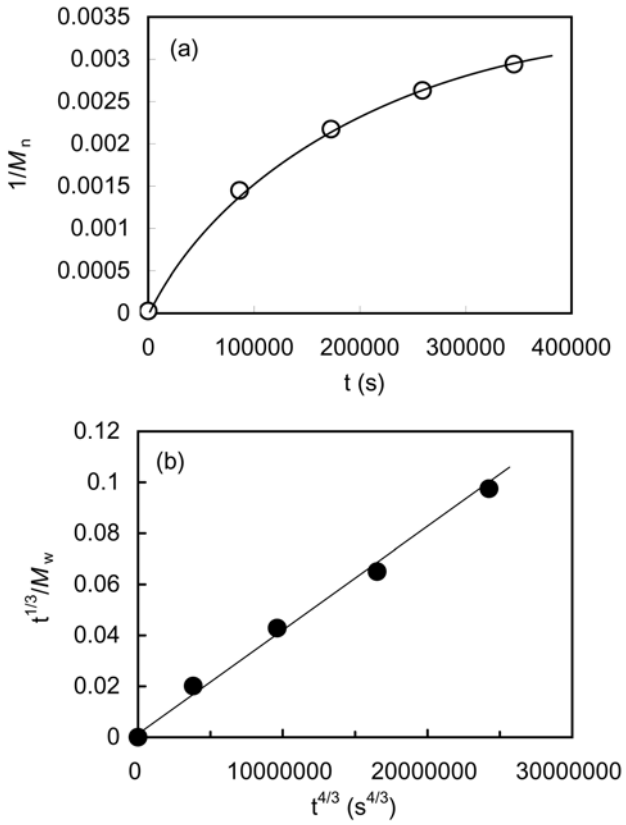

Figure 2. Plots of relationships between $1/M_n$ *vs.* time and $t^{1/3}/M_w$ *vs.* $t^{4/3}$ of PLLA during UV-C irradiation for 5 days.

Optical purity of lactate units in PLLA chains also decreased linearly under irradiation (Figure 3 and Table SI-1). It is clear, when compared against the constant values in the optical purity of reference samples, that the decreases in irradiated samples must be induced by the UV-C irradiation. To examine

the relationship between the decrease in optical purity and the chain scission, increase in chain-end number, which was calculated from initial M_{n0} and current M_n values, was plotted against increase in D-lactate unit (%) (Figure 4). The plot exhibited a relatively proportional relationship with the D-lactate unit being newly produced in a ratio of 0.30-0.41 per one scission, suggesting that chain scission and following reactions are related to racemization. This important finding fundamentally accords with the previous result of PLLA photolysis behavior in the initial period (0-120 min).[12]

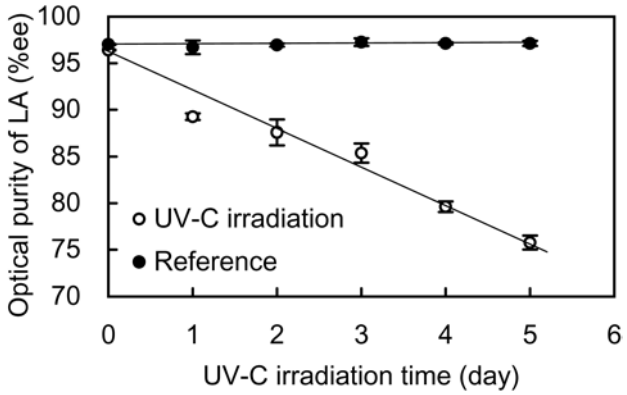

Figure 3. Changes in optical purity of lactate units in PLLA chains during UV-C irradiation for 5 days. Standard deviation values were shown by upper and lower bars.

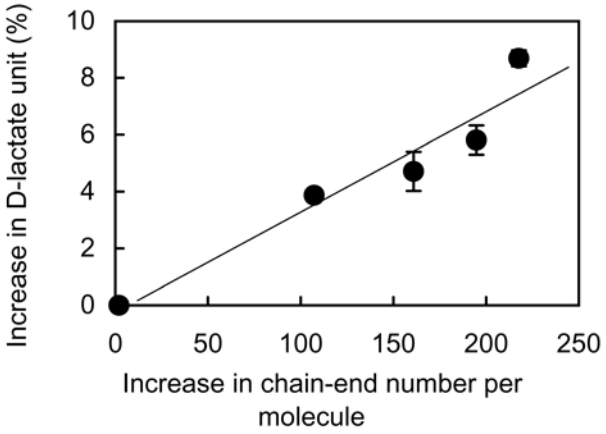

Figure 4. Relationship between increases in chain-end number and D-lactate unit. The numbers of chain-ends and D-lactate units were estimated from M_n values and HPLC analysis results of irradiated samples.

Changes in Stereoregularity during photolysis. The racemization of lactate units in a PLLA chain affects the stereoregularity of sequence. In Figure 5, a ^{13}C NMR spectrum of as-synthesized PDLLA (M_n 12000, M_w 26000, lactate unit ratio L/D=49.4/50.6) from D,L-lactide is shown. This spectrum profile is basically the same as that of previously reported spectra.[14,16] A typical signal for the isotactic sequence LLLLLL (*iiiii*) was detected at 169.58 ppm. Signals for chain-end racemized sequences LLLLLD (*iiiis*) and DLLLLL (*siiii*) appeared at lower magnetic fields than that of the isotactic sequence, while other racemized sequences having internal D-units were found at higher magnetic fields.

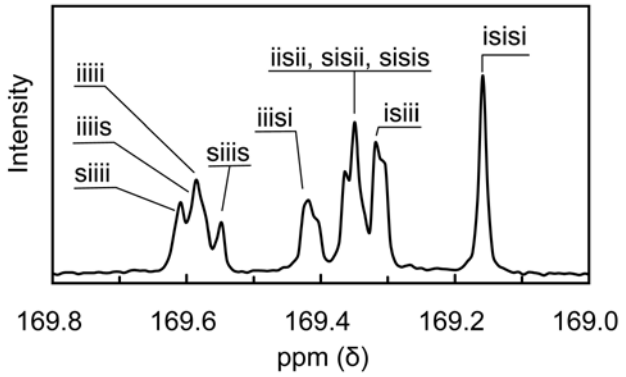

Figure 5. ^{13}C NMR spectrum of PDLLA.

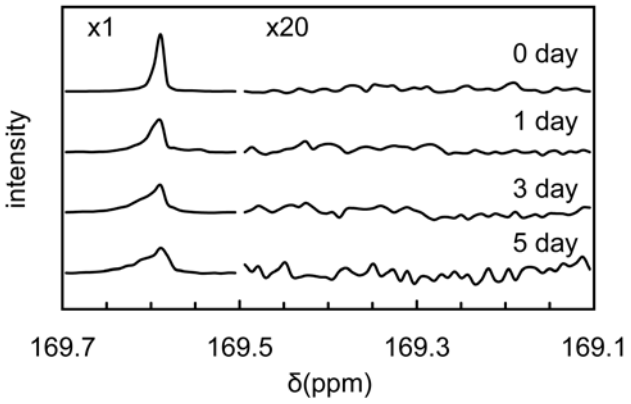

Figure 6. Changes in ^{13}C-NMR spectrum of PLLA film during UV-C irradiation.

To confirm the changes in the stereoregularity of PLLA chain sequence during the UV-C irradiation, ^{13}C NMR spectra of UV-irradiated samples were measured as shown in Figure 6, in which the plot in the high magnetic field area of 169.1-169.5 ppm is shown with intensity magnified 20 times compared

to the plot in the low magnetic field area of 169.5-169.7 ppm with no magnification. Certain changes were detected such as the appearance of shoulder peaks at magnetic fields lower than 169.58 ppm for the typical isotactic sequence LLLLLL, which increased in intensity with irradiation time. On the other hand, in the high magnetic field range, there were noisy signals, but no clear changes with time in spite of the 20× magnification in the intensity. This spectral feature of UV-irradiated PLLA samples indicates that the samples preferentially have racemized D-lactate units at chain-ends.

Using the Hartree-Fock method as a semi-empirical molecular orbital method, the chemical shift values of carbonyl carbons in the ^{13}C NMR spectrum of lactic acid hexamers were calculated. The hexamer has a molecular weight of 450 similar to the M_n of the irradiated samples shown in Figure 1 and Table SI-1 (see Supporting Information). Obtained chemical shift values of C(=O) at both $\pm_{OH}$ and $É_{COOH}$-terminal D-units for diastereoisomers: DLLLLL and LLLLLD are listed in Table 1 in comparison with the values of LLLLLL sequences. Interestingly, the chemical shift values of C(=O) in both terminal units were at lower magnetic fields than the values of the corresponding C(=O) in the original sequence LLLLLL. These results indicate that the shoulder peaks in the low magnetic field range of 169.5-169.7 ppm are assignable to terminal D-units.

The above results show that the photodegraded PLLA chains increased the racemized chain-end D-units as a function of irradiation time without increasing the internal D-units.

Table 1. Chemical shift values of chain-end carbonyl carbons in stereoisomeric hexamers calculated by the Hartree-Fock method.

Lactate unit in hexamer	$´_{C=O}$ (ppm)		
	LLLLLL	DLLLLL	LLLLLD
$\pm_{OH}$ terminal unit	172.62	174.21	-
$É_{COOH}$ terminal unit	164.23	-	165.44

Comparison of racemization behavior of photolysis with hydrolysis and thermal degradation. To make clear the aspects of racemization behavior during PLLA photolysis, change in stereoregularity was compared with changes during hydrolysis and thermal degradation. Three kinds of treated samples that had similar molecular weights (Table 2) were used for ^{13}C NMR analysis to compare their stereoregularity. The photolysis, hydrolysis, and thermal degradation were performed by UV-C ($»_c$ = 253.7 nm, 4.3 mW·cm^{-2}) at 34°C/33% RH for 30 min; by high pressure steam at 120°C/0.202MPa for 90 min, and in a nitrogen atmosphere at 200°C for 5 h, respectively. Although all the treated samples had close molecular weight values (M_n = 12000-13000, M_w = 27000-28000), the difference in their respective optical purity values was considerable and significant when compared to their standard deviation values. The optical purity of the hydrolyzed sample was unchanged after the treatment, maintaining its original value. However, the optical purity values of the photolyzed and thermal degraded samples certainly decreased from their original values.

Table 2. Samples for tacticity analysis treated by three degradation methods.

samples	M_n	M_w	optical purity (%)
original	39000	71000	97.0 (± 0.06)[a]
photolyzed	13000	27000	96.2 (± 0.12)
hydrolyzed	13000	27000	97.0 (± 0.12)
thermal degraded	12000	28000	95.8 (± 0.33)

[a] standard deviation.

Comparative ^{13}C NMR spectra of the treated samples are shown in Figure 7 with the original sample. In the spectra of the low magnetic field range (169.5-169.7 ppm), only the UV-irradiated sample exhibited shoulder peaks at lower magnetic fields than that of the isotactic hexad sequence peak at 169.58 ppm. Other samples showed only the isotactic peak similar to that of the original PLLA. In the spectra of the high magnetic field range (169.1-169.5 ppm) shown at 30 magnifications in intensity, only the thermally degraded sample developed clear multiple peaks assignable to other hexad sequences

including racemized internal D-units. However, the photolyzed and hydrolyzed samples exhibited no definite peak in the field area.

These characteristic features on the spectral changes during the degradation processes were confirmed by the time-course test of each treatment. In Figure 8 and 9, the spectral changes with the hydrolysis and thermal degradation time are shown, respectively. The changes in optical purity with treatment time are listed in Table SI-1 in Supporting Information. The time-course test of hydrolysis exhibited a little broadening of the LLLLLL sequence peak, but no obvious change was found in the high magnetic field range, suggesting that no racemization occurred, but that there are some effects of hydrolyzed chain-ends on the chemical shift. Contrastively, the time-course test of thermal degradation developed multiple peaks with treatment time assignable to internally racemized sequences, clearly demonstrating the racemization on internal units in a chain.

These results indicate that the preferential racemization behaviors of degradation processes: photolysis, hydrolysis, and thermal degradation are characteristic and distinct as being chain-end racemization, poor racemization, and internal-unit racemization, respectively. These characteristic racemization behaviors of the three kinds of treatments were first confirmed in this study.

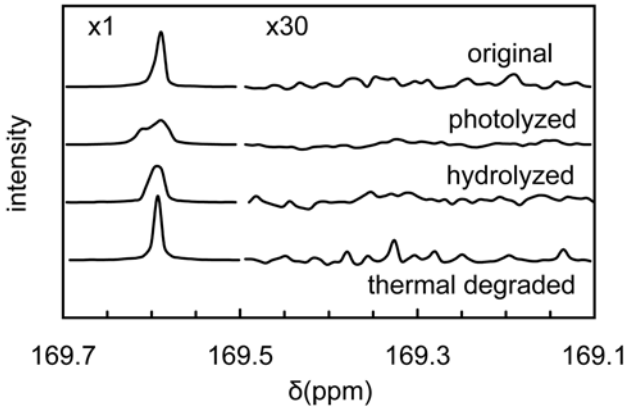

Figure 7. Comparative ^{13}C-NMR spectra of PLLA samples treated by photolysis, hydrolysis, and thermal degradation.

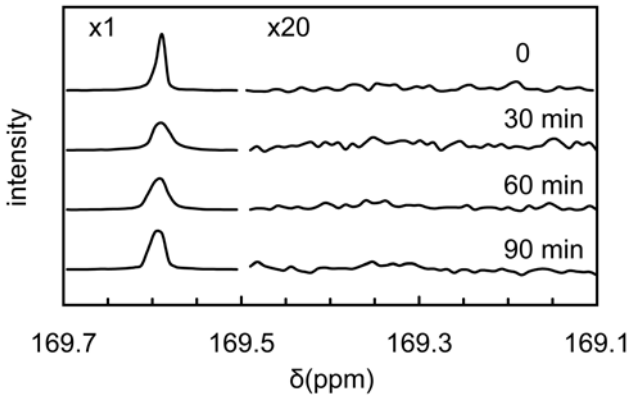

Figure 8. Changes in ^{13}C-NMR spectrum of PLLA film during hydrolysis by high pressure steam at 120°C/0.202MPa.

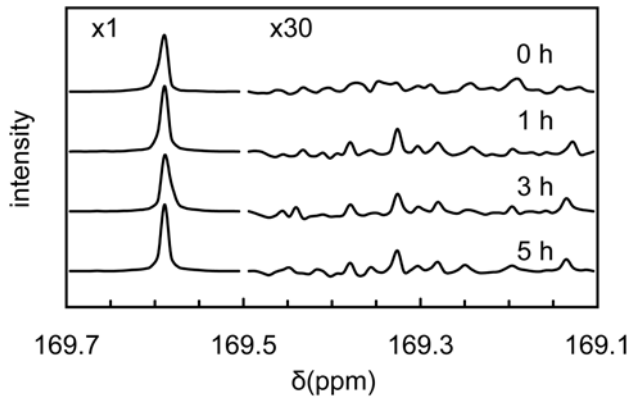

Figure 9. Changes in ^{13}C-NMR spectrum of PLLA film during pyrolysis in a nitrogen atmosphere at 200°C.

To quantitatively estimate changes in optical purity based on the increase in racemized D-unit, the amount of D-lactate unit was evaluated with HPLC analysis after complete ammonolysis. Estimated optical purity values are listed in Table SI-1. Taking into consideration the standard deviation values, the optical value certainly decreased during the photolysis and thermal degradation, whereas decrease in optical value was suppressed during the hydrolysis. The results in Table SI-1 support the above discussion quantitatively.

CONCLUTIONS

To clarify aspects of PLLA photolysis, the relationship between chain scission and racemization was examined. The hexad stereosequential analysis of photodegraded PLLA was investigated to specify the racemized positions within a chain in comparison to those of hydrolysis and thermal degradation. From kinetic analyses of photolysis, it was estimated that the degradation proceeded in a manner of the non-autocatalytic random degradation kinetics, and it was suggested that the racemization occurred in proportion to the number of chain scissions. From ^{13}C NMR analysis, the UV-irradiated PLLA samples were shown have racemized D-lactate units most frequently at chain-ends. In a comparison of the racemization behavior among photolysis, hydrolysis, and thermal degradation, it was confirmed that the features of racemization behavior during the degradation processes are characteristic and distinct from each other, being chain-end racemization, poor racemization, and internal-unit racemization, respectively.

Supporting Information Available: Changes in optical purity during photolysis, hydrolysis, and thermal degradation of PLLA are listed in Table SI-1. This material is available free of charge via the Internet at http://pubs.acs.org.

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